

# Removal of Heavy Metals from Mine Waters by Natural Zeolites

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In this study, we investigated the removal of Fe, Pb, Cd, and Zn from synthetic mine waters by a natural zeolite. The emphasis was given to the zeolite's behavior toward a few cations in competition with each other. Pb was removed efficiently from neutral as well as from acidic solutions, whereas the uptake of Zn and Cd decreased with low pH and high iron concentrations. With increasing Ca concentrations in solution, elimination of Zn and Cd became poorer while removal of Pb remained virtually unchanged. The zeolite was stable in acidic solutions. Disintegration was only observed below pH 2.0. Forward- and back-titration of synthetic acidic mine water were carried out in the presence and absence of zeolite to simulate the effects of a pH increase by addition of neutralizing agents and a re-acidification which can be caused by subsequent mixing with acidic water. The pH increase during neutralization causes precipitation of hydrous ferric oxides and decreased dissolved metal concentrations. Zeolite addition further diminished Pb concentrations but did not have an effect on Zn and Cd concentrations in solution. During re-acidification of the solution, remobilization of Pb was weaker in the presence than in the absence of zeolite. No substantial differences were observed for Fe, Cd, and Zn immobilization. The immobilization of the metals during pH increase and the subsequent remobilization caused by re-acidification can be well described by a geochemical equilibrium speciation model that accounts for metal complexation at hydrous ferric oxides, for ion exchange on the zeolite surfaces, as well as for dissolution and precipitation processes.

## Introduction

The release of heavy metals into terrestrial and aquatic ecosystems can be mainly attributed to human activities (1). Mining of ore deposits that contain large amounts of sulfide minerals and heavy metals is an important source of heavy metals in the environment (2, 3). The main pathways include airborne distribution of polluted dust from mine tailings or waste rock piles and discharge of acid mine drainage waters. As a result of oxidation of pyrite (FeS<sub>2</sub>) or pyrrhotite (FeS), pH value in the affected soil and water body may drop below

pH 4 (4, 5), leading to the solubilization of heavy metals including Pb, Cd, Zn, Cu, Cr, Ni, and Fe (2).

Acid mine drainage waters are usually treated by adding alkaline materials such as lime, fly ash, or alkaline industrial wastes to precipitate metals as hydroxides (4, 6). Major disadvantages of this method are the need for continuous addition of the amendment, low reaction rates, and the production of huge amounts of secondary wastes (2, 7). The binding form is of primary importance for the long-term stability of immobilization. The uptake of heavy metals onto low-cost sorbents, e.g., naturally occurring zeolites, is seen as an alternative to the mentioned treatment techniques. Similar to clay minerals, isomorphous substitution of Si by Al in the three-dimensional lattice of the zeolite is the cause of a net negative charge, which is balanced by exchangeable cations. In contrast to synthetic zeolites, natural zeolites exhibit, in general, a higher resistance toward acidic solutions. Among the 40 known natural zeolite minerals, clinoptilolite is one of the most abundant. It is found in large deposits and mined all over the world (8, 9), although high-quality deposits are not often found. Due to its low density and extraordinary properties it is widely used (10–13). In particular, it has a high selectivity for NH<sub>4</sub><sup>+</sup>, Cs<sup>+</sup>, and Sr<sup>2+</sup> and certain heavy metals, and is used for the treatment of wastewater and contaminated soils, as well as for agronomical applications (9, 14, 15). Selectivity series have been given as Pb<sup>2+</sup> > NH<sub>4</sub><sup>+</sup>, Ba<sup>2+</sup> > Cu<sup>2+</sup>, Zn<sup>2+</sup> > Cd<sup>2+</sup>, Sr<sup>2+</sup> > Co<sup>2+</sup> by Blanchard et al. (16) and as Pb<sup>2+</sup> > Cd<sup>2+</sup> > Cs<sup>+</sup> > Cu<sup>2+</sup> > Co<sup>2+</sup> > Cr<sup>3+</sup> > Zn<sup>2+</sup> > Ni<sup>2+</sup> > Hg<sup>2+</sup> by Zamzow et al. (17). The high selectivity for toxic metals such as Pb, Cd, and Zn makes clinoptilolite a promising material for the treatment of mine wastewaters.

To increase the exchange capacity of zeolites, and because the determination of isotherms requires an exchanger with homoionic structure, many studies have been conducted with pretreated zeolite materials (16, 18–22). Although in practice it is desirable to minimize pretreatments, only a few studies used untreated ("as-received") clinoptilolite samples (23, 24). Further, only few data are available on the stability of clinoptilolite in acidic solutions, as relevant for mine wastes. Carland and Aplan (25) and Inglezakis et al. (26) found that uptake of heavy metals by zeolite is limited at low pH. Grain size is another important, but rarely studied factor to be considered in the application of zeolite material (20, 21, 27, 28). Most important, little is known about the influence of competing cations on the performance of zeolites in wastewater treatment (17, 23, 29). In one of the few studies on acid mine water treatment by means of zeolites, Moreno et al. (6) showed that zeolites synthesized from coal fly ash effectively removed heavy metals. In another study, Zamzow et al. (17) compared different zeolite types with respect to heavy metal uptake from simulated wastewater and found that Ca concentration limited the uptake of heavy metals.

The current study focused on the influence of pH and grain size on the efficiency of clinoptilolite to remove heavy metals from mine waters, with the emphasis on the zeolite's behavior toward divalent cations in competition with each other. For this purpose, we used a natural, untreated clinoptilolite containing tuff from Slovakia and artificially prepared metal solutions with low pH and high sulfate and iron concentrations. We also investigated the influence of zeolites on metal mobility during a conventional neutralizing treatment for acid mine waters and subsequent re-acidification. Forward- and back-titrations were carried out to simulate the effects of alkaline treatment and subsequent re-acidification on metal immobilization in the presence and absence of zeolite. Precipitation and remobilization of heavy

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**TABLE 1. Composition of Synthetic Mine Waters<sup>a</sup>**

	acidic mine water (mg/L)	weakly acidic mine water (mg/L)
Pb	3.8–4.9	9.7–10.3
Cd	5.0–5.3	5.2
Zn	47.5–49.1	40.1–42.4
Fe	526.8–600.1	no Fe
Ca	no Ca	0, 52.8, 233.4, and 448.4
pH	2.24	5.55

<sup>a</sup>For each set of experiments the synthetic mine waters were prepared fresh, leading to slight variations in concentration of metal cations in the mine waters.

metals were modeled with the hydrogeochemical speciation program PHREEQC (30).

## Materials and Methods

**Chemicals and Sorbent Materials.** All chemicals used were of reagent grade. The synthetic solutions were prepared from ZnCl<sub>2</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O, CaNO<sub>3</sub>, PbCl<sub>2</sub>, and CdCl<sub>2</sub>. The pH was adjusted with sulfuric acid. Natural zeolite from Nizný Hrabovéc (Slovakia) was used. The material was provided by Unipoint AG Truttikon (Switzerland). The grain size fractions were used as received from the company: 2.5–5.0 mm (fraction I), 1.0–2.5 mm (fraction II), 0.3–1.0 mm (fraction III), and <0.3 mm (fraction IV).

**Characterization of the Zeolite.** *Composition and Cation Exchange Capacity.* The chemical composition of the zeolite material was determined by fluorescence spectroscopy using a Spectro X-Lab 2000 X-ray instrument. The mineralogical composition was determined by XRD (Bruker AXS D8) and the data were analyzed according to the Rietveld method (program AutoQuan, GE Seifert). The cation exchange capacity was determined using the ammonium acetate method as described by Mackenzie (31).

*Acid Stability.* Aliquots of 0.33 g of zeolite (fraction IV) were mixed with 50 mL of distilled water. Then pH was adjusted by adding 0.1 M HNO<sub>3</sub>. After 24 h, the solutions were filtered through 0.45- $\mu$ m syringe filters and the aluminum concentration in the supernatant solution was determined by AAS.

In a second series of tests, 8-g samples of zeolite (fraction II) were suspended in 80 mL of acid solution at pH 1.0 and 2.2 for one week. The pH was controlled by measuring several times a day and adjusting with 1 M HCl if necessary. After one week, the samples were dried and ground and their mineralogical composition was analyzed by X-ray diffraction.

**Batch Ion Exchange Studies.** For ion exchange studies, two different synthetic mine waters were prepared. The chemical composition of these “mine waters” is presented in Table 1.

*Effects of pH and Grain Size Heavy Metal Uptake.* In each batch, 1 g of zeolite was mixed with 50 mL of acidic or weakly acidic mine water in a polyethylene bottle. After 7, 25, 48, and 168 h for the acidic mine water and 2, 19, 48, and 168 h for the weakly acidic mine water, the supernatant solutions were filtered through 0.45- $\mu$ m syringe filters and metal concentrations were determined with atomic adsorption spectrometry. All experiments were carried out in triplicate with appropriate blanks. For clarity, only the mean values are presented in the graphs. The standard deviations in general did not exceed 5% of the respective means.

*Effects of Competing Cations.* Samples of 1 g of zeolite were mixed with 50 mL of weakly acidic mine water, to which 50, 250, or 500 mg/L Ca had been added, in flasks and shaken for 2, 19, 48, or 168 h. The supernatant solutions were filtered and their metal concentrations were determined as described above. Again, all experiments were carried out in triplicate.

**TABLE 2. Chemical Composition (%) of the Zeolite Material (Water Content Approximates 4%)**

SiO <sub>2</sub>	70.90	MnO	0.004
Al <sub>2</sub> O <sub>3</sub>	10.49	Na <sub>2</sub> O	<0.2
CaO	2.82	K <sub>2</sub> O	3.58
MgO	0.92	SO <sub>3</sub>	<0.005
TiO <sub>2</sub>	0.12	Fe <sub>2</sub> O <sub>3</sub>	1.35
P <sub>2</sub> O <sub>5</sub>	0.004		

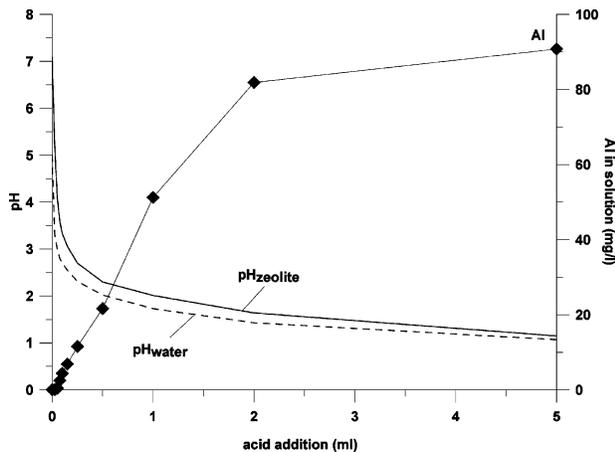
*Effects of Re-Acidification.* In conventional acid mine water treatment, including neutralization and oxygenation, the process time is about 30 min. Accordingly, duration of 15 min was chosen for this experiment. Samples of 1 g of zeolite (fraction III) were mixed with 50 mL of acid mine water each. Then the pH was adjusted to values of 2.5, 3.0, 3.5, 4.0, 5.0, 6.0, or 7.0 by adding 0.1 and 0.01 M NaOH over a time of 15 min under constant stirring. For comparison the same experiment was performed without zeolite addition. After the desired pH was reached a sample of 10 mL was taken.

In a second experiment 2 g of zeolite was added to 100 mL of acid mine water. Then the pH of the suspension was adjusted to a value of 7.0 with 0.1 and 0.01 M NaOH. After forward titration, a sample of 10 mL was taken. The remaining solution was back-titrated to pH 2.5 with 0.1 M HNO<sub>3</sub>. A sample of 10 mL was taken immediately after the titration. In both experiments, all samples were filtered through 0.45- $\mu$ m syringe filters and analyzed for their metal concentration using AAS. The changes in volume caused by addition of base or acid and by taking of samples were considered.

*Modeling of Chemical Speciation.* Both experimental series were modeled using PHREEQC (30), which calculates the expected equilibrium states of the system: aqueous solution—mineral phases—gas phases, including speciation, surface complexation, precipitation, and dissolution. As any kinetics, Fe<sup>2+</sup> oxidation was not included in the model. The conceptual model is illustrated in Figure S1 (Supporting Information). In a first step, the initial composition of the synthetic mine water was calculated for the presence of melanterite [FeSO<sub>4</sub>·H<sub>2</sub>O], ZnCl<sub>2</sub>, PbCl<sub>2</sub>, and CdCl<sub>2</sub>. The pH was adjusted by H<sub>2</sub>SO<sub>4</sub>. The concentration of total inorganic carbon was calculated for equilibrium with CO<sub>2</sub>(g) at a partial pressure of 10<sup>-3.5</sup> atm. Then, NaOH and O<sub>2</sub> were added in 23 steps of individual amounts to match pH and iron concentration as close as possible. For each step, equilibrium was calculated including solids such as ferrihydroxides, metal hydroxides, and carbonates. All mineral phases that were considered to be in thermodynamic equilibrium with the aqueous solution are listed in Figure S1 (Supporting Information). The solids were not present initially but formed by precipitation. After iron hydroxides started to precipitate, metal uptake by surface complexation on these precipitates was also taken into account. For the calculation of surface complexation reactions, the generalized two-layer model described by Dzombak and Morel (32), which defines two types of binding sites (strong and weak), was used. Surface precipitation was not considered in the calculations. The thermodynamic constants for the reactions and the surface complexation model were taken from the WATEQ4F database (33), which is included in PHREEQC (30).

## Results and Discussion

**Characterization of the Zeolite.** Table 2 shows the chemical composition of the zeolite used throughout the experiments. Rietveld analysis of XRD data reveal that the zeolite material consisted of 79 ± 2% clinoptilolite, 9 ± 1% illite, 6 ± 1% cristobalite, 3 ± 0.3% quartz, and 3 ± 0.9% plagioclase. The cation exchange capacity was measured to be 1.47 mequiv/g, and the exchanged cations were 0.45 mmol Ca, 0.52 mmol K, 0.040 mmol Mg, and 0.013 mmol Na per g zeolite material.



**FIGURE 1.** Development of pH and dissolved aluminum after addition of nitric acid.

The clinoptilolite content and the cation exchange capacity of our material are typical for zeolites from sedimentary deposits (34), although some natural zeolite deposits contain material with higher cation exchange capacities. Clinoptilolite accounts for most of the cation exchange capacity, while illite contributes to a small degree only.

**Acid Stability.** Dissolved aluminum concentrations and pH after 24 h are shown in Figure 1. In the presence of zeolite the pH was up to 2 units higher than that in the solid free solutions, indicating the buffer capacity of the material. Aluminum concentrations in solution markedly increased only after the pH dropped to values below 2.0, indicating dissolution of the material below this value. As the material

was not composed of clinoptilolite alone, but also contained feldspar and muscovite, it is not possible to specify which of the phases dissolved to what extent.

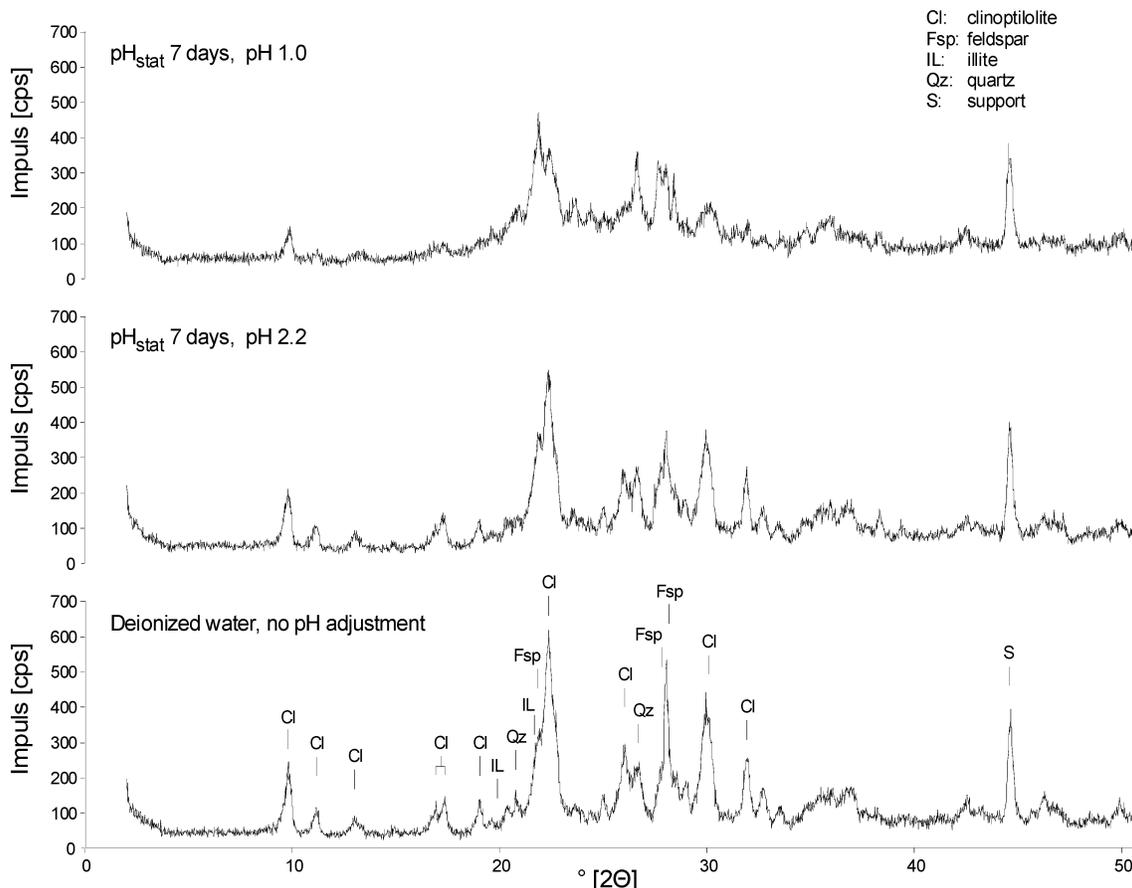
The XRD spectra (Figure 2) show that the feldspar and the illite peaks were reduced after the zeolite material had been exposed to pH 2.2 for one week, whereas the clinoptilolite peaks remained almost unchanged. At a solution pH of 1, all peaks were clearly diminished. The clinoptilolite peaks were still recognizable, but clearly influenced by the acidic solution. These findings are in good agreement with the observed increase in dissolved Al concentrations below pH 2.0. Carland and Aplan (25) found that clinoptilolite rich samples from Hector, California, dissolved only in solutions with a pH below 1. In contrast to our experiment, the contact time in their experiment was only 48 h.

**Effects of Grain Size and pH on Heavy Metal Uptake.**

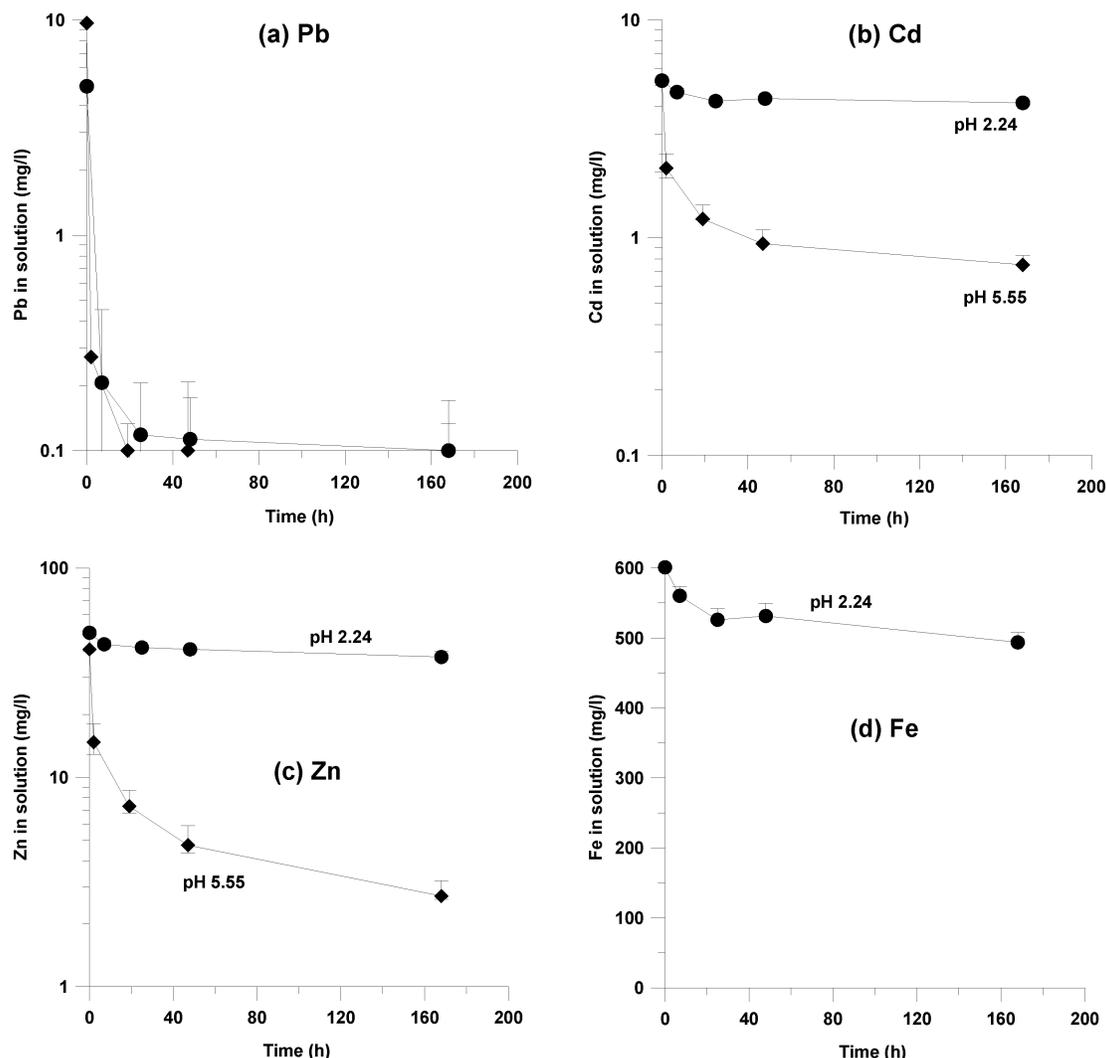
Grain size had only a very small effect on heavy metal uptake (Figure 3). In general, smaller particles bind slightly more heavy metals than coarser ones, especially at the beginning of the experiment. This is in agreement with the findings of Malliou et al. (20) and Maliou et al. (21) who found no substantial difference in metal uptake by zeolites of different grain sizes after 70 h. At shorter contact times they found that more Pb and Cd were sorbed, however, by fine-grained zeolite than by coarse-grained zeolite.

Figure 3 shows that the solution pH had a strong influence on Zn and Cd uptake but little effect on Pb uptake. Removal of Pb from the solution was almost complete at pH 5.5 (99.9%) as well as at pH 2.2 (99.5%). Zn removal decreased from 93.6% in weakly acidic water to 23.4% in acidic water. For Cd the removal percentages were 85.8% and 21.0%, respectively.

Limited metal uptake at low pH can be attributed to increased competition for sorption sites with protons. Carland



**FIGURE 2.** XRD analysis of untreated and acid-treated zeolite samples. Duration of experiment was 7 days. The pH value was kept constant with 1 M HCl.



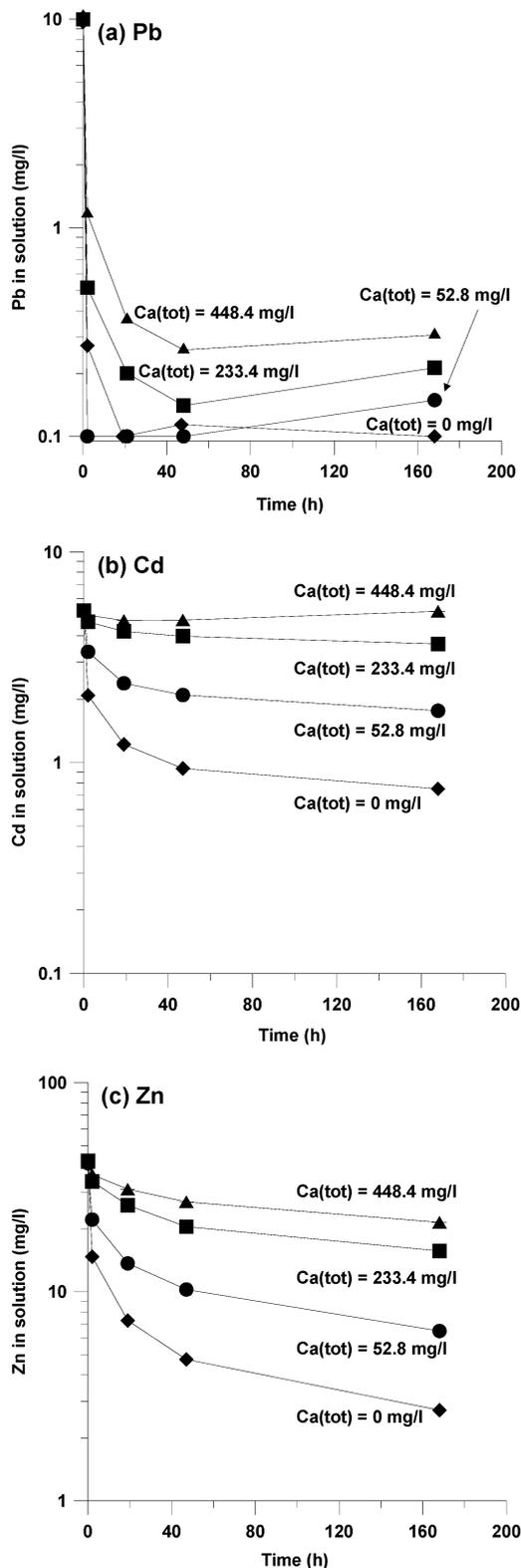
**FIGURE 3.** Metal concentrations in acidic mine water (pH 2.24, Cd = 5.3 mg/L, Pb = 4.9 mg/L, Zn = 49 mg/L, Fe = 600 mg/L) and weakly acidic mine water (pH 5.55, Cd = 5.3 mg/L, Pb = 9.7 mg/L, Zn = 41 mg/L, no Fe). The first data point marks the initial metal concentration in the mine waters. The following points show the metal concentration in solution after addition of 1 g/50 mL zeolite of grain size Fraction II (1–2.5 mm). Bars represent the maximal positive and negative deviation of the heavy metal concentrations in solution for other grain sizes that were used.

and Aplan (25) found that Cu uptake by a clinoptilolite-containing tuff was significantly decreased at pH values below 4. Ouki and Kavannagh (35) showed that Cu, Cr, Ni, Co, Zn, and Cd uptake by clinoptilolite was reduced at low pH, whereas Pb uptake remained almost unchanged. Metal uptake by clinoptilolite was also found by Inglezakis et al. (26) to be particularly pH dependent for those metals which are not specifically bound.

The Fe(II) concentration in the acid mine water was 15 and 230 times higher than Zn and Cd concentrations, respectively. The zeolite sorbed up to 18.3% of the Fe(II) from the initial acid mine water. It is possible that the high Fe(II) concentrations could have led to limited Zn and Cd uptake by competition for sorption sites. No selectivity data for Fe(II) and clinoptilolite was found in the literature. Loizidou (36) found higher selectivity for Pb, Zn, and Cd than for Fe(III), indicating that the uptake of these metals should not be negatively influenced by Fe(III). However, because hydrated diameters and Gibbs free energies of hydration of Fe(II) (5.82 Å, -1840 kJ/mol) and Fe(III) (7.06 Å, -4265 kJ/mol) (37) are different, these findings cannot be compared directly to those of our experiment. The effect of different hydration energies on selectivity of the zeolite for the examined metals will be discussed in a subsequent section.

Note that the presence of illite, even at low proportions, may have a significant impact on metal adsorption. Under highly acidic pH, adsorption of metals onto illite might be avoided due to protonation of surfaces; however, at pH > 5 the surface adsorption efficiency progressively increases.

**Effects of Competing Cations.** The effect of competing Ca on the uptake of Pb, Zn, and Cd is shown in Figure 4. Uptake of Pb was only slightly influenced, whereas Zn and Cd uptake decreased strongly with increasing Ca concentrations, which is comparable with the results of Kesraoui-Ouki and Kavannagh (29). These findings can be explained by different preferences of the clinoptilolite for different cations. Because of its high Si:Al ratio, clinoptilolite has a low structural charge density. Therefore, divalent cations with low hydration energies are sorbed preferably compared to cations with high hydration energies (38). The Gibbs free energies of hydration are -1425 kJ/mol for Pb, -1505 kJ/mol for Ca, -1755 kJ/mol for Cd, and -1955 kJ/mol for Zn (37). This explains why Pb uptake was only slightly influenced by Ca competition, whereas Cd and Zn uptake was significantly reduced at high Ca concentrations. According to the hydration energies, the zeolite will also prefer Pb over Cd and Zn in mixed metal solutions. Therefore, it is to be expected that high Pb concentrations will limit the uptake of Cd and Zn. Additionally, the comparison of Zn and Cd Gibbs free energies of



**FIGURE 4.** Influence of Ca concentration on Pb (a), Cd (b), and Zn (c) sorption by zeolite. The initial metal concentrations were Cd =  $5.25 \pm 0.05$  mg/L, Pb =  $10.0 \pm 0.3$  mg/L, and Zn =  $41.6 \pm 0.8$  mg/L.

hydration with those of Fe(II) suggests that Zn uptake could, whereas Cd uptake should not, be negatively influenced by Fe(II) in the solution. In addition to the conditions chosen in our experiments, one has to bear in mind that Ca, Mg, and Mn concentrations in acidic waters may reach high values and that this may reduce the metal uptake efficiency.

**Effects of Re-Acidification.** Figure 5 shows the effect of neutralization and re-acidification on heavy metal concentrations in solution in the absence and presence of zeolite. When pH was increased by NaOH addition, the precipitation of a reddish phase was observed in both experimental setups. With further pH increase above 5 these reddish precipitates gradually changed color and became dark greenish at pH 7. As Figure 5 shows, the dissolved concentrations of all four heavy metals, i.e., Fe, Pb, Zn, and Cd, decreased with increasing pH. Dissolved Fe, Zn, and Cd concentrations differed only slightly between the samples with and without zeolite at pH values below 5. Pb concentrations were much lower in the presence than in the absence of zeolite under acidic conditions. Above pH 5 the samples without zeolite exhibited higher dissolved metal concentrations than those with zeolite. Around pH 6, about twice as much Zn, Cd, and Fe remained dissolved in the zeolite-free samples in comparison to the samples with zeolite, while Pb was almost completely sorbed under both conditions. At pH 7, also Zn was sorbed in both experimental systems. Surprisingly, dissolved Fe and Cd concentrations did not further decrease in suspensions with zeolite when pH increased from 6 to 7, whereas they steeply dropped in the absence of zeolite. Thus at pH 7, much more Cd and Fe was kept in solution in the presence than in the absence of zeolite. During re-acidification the concentrations of Fe, Cd, and Zn in solution reached values close to the initial concentrations in the acidic mine water, both in the samples without zeolite and those with zeolite. In contrast, the Pb concentrations increased only slightly in the samples with zeolite, suggesting that the zeolite was able to retain the Pb cations (Table 3).

In a first model run using PHREEQC, the amount of precipitated hydrous ferric oxides was calculated without consideration of surface complexation. In the next runs, surface complexation was taken into account using the amount of hydrous ferric oxides as obtained from the previous run. The iteration procedure was carried out until convergence was reached. In Figure 5, the simulated metal concentrations are compared with experimental values. According to the model,  $\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$  (39) is the most important iron phase in the presence and absence of zeolite and is precipitating over the entire experimental pH range. The oxidation of Fe(II) to Fe(III) leads to a sharp drop of dissolved iron between pH 6 and 7 for samples without zeolite (Figure 5d). This drop is related to the precipitation of amorphous  $\text{Fe}(\text{OH})_3$  (39) that acts as adsorbent for Cd and Zn. If surface complexation on iron hydroxides was not taken into account, the model predicted that Pb remained in solution up to pH 6.5–7.0. In this pH range, Plattnerite ( $\text{PbO}_2$ ) started to precipitate as well as Otavite ( $\text{CdCO}_3$ ) and amorphous ZnO. To represent the measured heavy metal concentrations, surface complexation reactions had to be taken into account. This strongly suggests that surface complexation at iron hydroxides was crucial for metal immobilization in the absence of zeolite.

For the modeling of the experiments with zeolite (solid lines in Figure 5), an exchanger phase had to be included in addition to the specific sorption sites provided by the iron hydroxides. Zeolites have exchange sites with different positions in the lattice and thus different bond energies. Steric hindrance and unfavorable charge distributions can affect extent and kinetics of cation exchange in zeolites (38). To account for the inaccessibility, the exchange capacity of the zeolite material was limited to 1 mequiv/g. The initial ratio of exchangeable cations (Ca, Mg, K, Na) were set as experimentally obtained. The equilibrium constants for the exchange reactions were fitted under consideration that they are valid only for the defined experimental conditions. Immobilization of Pb after pH increase was more effective when zeolite was added. Measured and modeled data clearly

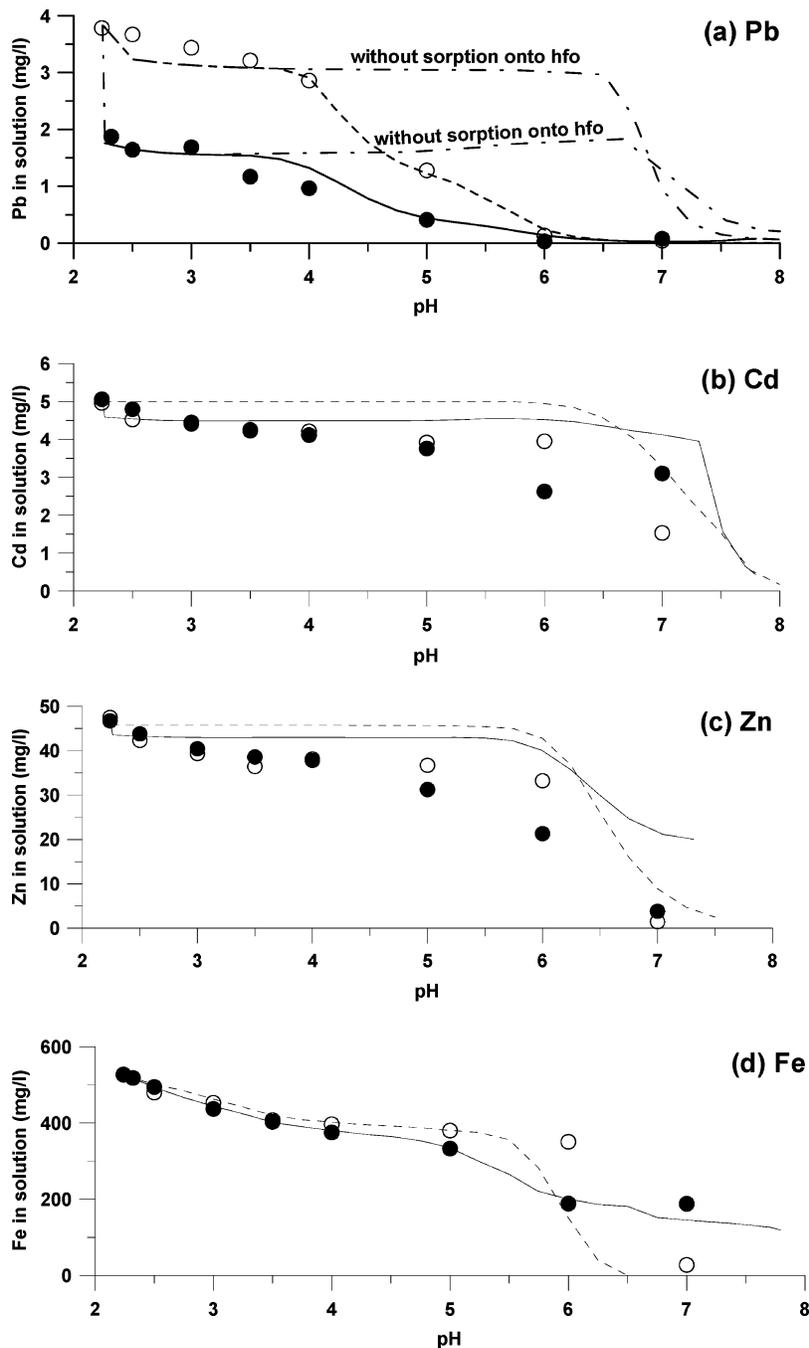


FIGURE 5. Immobilization of Pb (a), Cd (b), Zn (c), and Fe (d) with increasing pH during NaOH addition in single batches in the absence (open symbols) and presence (filled symbols) of zeolite. The initial metal concentrations were Cd = 5.0 mg/L, Pb = 3.8 mg/L, Zn = 47.5 mg/L, and Fe = 527 mg/L. Symbols represent experimental values, and lines show modeled curves. In (a) modeled curves without consideration of sorption onto hydrous ferric oxides (hfo) are also shown.

	without zeolite		with zeolite (20 g/L)	
	experimental	modeled	experimental	modeled
pH	2.5	2.5	2.6	2.5
Fe (mg/L)	451.2	524.1	386.5	524.1
Pb (mg/L)	2.9	3.8	1.0	2.1
Zn (mg/L)	50.4	45.7	41.4	44.3
Cd (mg/L)	5.4	5.0	4.7	4.7

show that Pb was preferentially bound by exchange reactions, whereas Fe, Zn, and Cd were affected little below pH 6.

In the presence of zeolite, the first decrease in the modeled Fe concentration at pH 5 is due to precipitation of amorphous  $\text{Fe}(\text{OH})_3$ . The following flattening of the curve represents the dissolution of amorphous  $\text{Fe}(\text{OH})_3$  and the beginning of  $\text{Fe}_3(\text{OH})_8$  (40) precipitation, which leads to further decrease of Zn and Cd through adsorption above pH 6.75. In the presence of zeolite the amount of precipitated  $\text{Fe}(\text{OH})_3$  is approximately 10 times less than that in absence of zeolite. Therefore, more Fe remains in solution and is forming  $\text{Fe}_3(\text{OH})_8$ . The exchange constant for Fe and zeolite was lower than the ones for the heavy metals. Some Fe was precipitated as  $\text{Fe}_3(\text{OH})_8$  that contained  $\text{Fe}^{2+}$  as well as  $\text{Fe}^{3+}$ .

In reality, the higher dissolved  $\text{Fe}^{2+}$  concentration in the presence of the zeolite may be caused by surface acidity of

the zeolite. The oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> is not only dependent on pH, but also on the oxygen content of the system. Below pH 5, the oxidation kinetics is slow, taking several orders of magnitude longer than our neutralization experiments, and can be assumed to be pH independent. Above pH 5, the oxidation kinetics is pH dependent and the rate law is second order with respect to the activity of OH<sup>-</sup> ions (40). The higher concentrations of Fe and Cd in the zeolite-containing samples may be caused by surface acidity of the zeolite (41, 42) and therefore slow the oxidation of Fe<sup>2+</sup>, formation of Fe hydroxides, and removal of Fe and Cd from the solution. For Zn the same probably occurred between pH 6 and 7, where no sample was taken. Quantification of surface acidity was not carried out in the experiments.

Re-acidification to pH 2.5 was simulated by adding HNO<sub>3</sub> in one step to the neutralized mine water in the presence and absence of zeolite. Again, the system was assumed to reach equilibrium and surface complexation reactions were taken into account. Measured and simulated dissolved metal concentrations are given in Table 3. The model provided a good description of the experimental data for neutralization as well as for re-acidification. It was possible to show that surface complexation by hydrous ferric oxides as well as ion exchange on the zeolite phase were the main mechanisms accounting for the reduction of heavy metal concentrations in the solutions, especially for Pb. For Zn and Cd the modeled curves overestimated the experimental data. A possible reason is that the model underestimates the capacity and affinity of the precipitated Fe hydroxides. The model also does not account for solid solution phenomena.

The composition of the solution after re-acidification was well-predicted by the model. Zn and Cd concentrations increased independently of zeolite as in the original mine water (Table 3). In contrast, Pb concentrations remained significantly lower if zeolite was added, showing that addition of zeolites can effectively limit remobilization of Pb.

## Acknowledgments

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## Supporting Information Available

Flow chart showing the different calculation steps of the hydrogeochemical model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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